WATER RESOURCES RESEARCH GRANT PROPOSAL

Project ID: 2002AZ9G

Title: Agricultural Chemicals as a Major Non-Point Source of Arsenic: Microbial Transformation of Organic Arsenicals

Project Type: Research

Focus Categories: Toxic Substances, Agriculture, Non Point Pollution

Keywords: Organic arsenicals, biotransformation, biodegradation, pesticide, arsenic, metabolite, detection

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Abstract

Lowering the public health risks associated with the intake of arsenic (As) is a national priority. EPA has enacted a new drinking water standard for As (10 parts per billion). Arsenic is a naturally occurring element in rocks and can be liberated into soil and water upon weathering. In addition to natural sources, large quantities of As can enter into the environment as organo-arsenic compounds through agricultural activity. Monosodium methanearsonic acid (MSMA), disodium methane-arsonic acid (DSMA) and cacodylic acid (CA) are utilized as herbicides in cotton; whereas roxarsone (3-nitro-4-hydroxyphenylarsonate) is utilized as feed additive/ antibiotic agent in poultry farming. The national annual discharge of MSMA and roxarsone into the environment are estimated at 2.6 million and 1.2 million kg, respectively. The non-point pollution of organo-arsenic compounds from agricultural may have an important impact on As budgets in ground- and surface water. In order to monitor and predict the fate of organic arsenicals in the environment, the major biotransformation products expected from the microbial conversion of these agricultural chemicals should be understood. The goal of this project is to identify major metabolites accumulating in the environment from the bioconversion of agricultural organic

arsenicals (i.e., MSMA, DSMA, CA, and roxarsone), evaluate their toxicity and establish analytical protocols for their detection. Microbial processes and microorganisms responsible for key conversions will be studied to gain better insight on the mechanisms responsible for the biotransformation of organic arsenicals. The project will be divided into seven tasks that are grouped into three thrusts: thrust A (tasks 1-4) "biotransformation"; thrust B (tasks 5-6)"toxicity"; and thrust C (task 7) "detection". In tasks 1 and 2, the biotransformation of MSMA, CA and roxarsone will be evaluated in anaerobic and aerobic enrichment cultures. Organic arsenicals will be tested as carbon and energy sources as well as electron acceptors. Metabolites formed will initially be quantified and identified by ion chromatography - inductively coupled plasma - mass spectrometry (IC-ICP-MS) or high perfomance liquid chromatography - diode array detector (HPLC-DAD), gas chromatography - mass spectrometry (GC-MS). If further structural elucidation is required, fractions collected by preparative HPLC will be characterized by MS-MS and nuclear magnetic resonance spectroscopy (NMR). The possible formation of As-containing humic polymers from roxarsone will be monitored by size exclusion chromatography. Task 3 will evaluate the fate of the organic arsenicals in soil microcosms by monitoring the aqueous-extractable, soil-bound and volatile As-species. Task 4 will investigate the fate of roxarsone in poultry manure compost to determine the impact of manure storage management practices on As speciation. The toxicity of microbial incubates and identified biotransformation products will be evaluated in tasks 5 and 6. Finally in task 7, protocols that are presently being developed at USGS for the detection of organo-arsenic compounds will be modified to include the analysis of newly identified biotransformation products.

The information obtained in the project will provide the basis for detecting and predicting the fate of agricultural organic arsenicals in the environment. Upgraded analytical protocols can be used by the USGS in ongoing and future efforts to monitor pesticide residues and As in the environment. The identification of biotransformation products and their preliminary toxicity testing will also provide insight on the public health risks associated with the use of organo-arsenicals in agriculture.